# Accepted Manuscript

Trialkylsilylethynyl-substituted triphenylenes and hexabenzocoronenes: highly soluble liquid crystalline materials and their hole transport abilities

Takuji Hirose, Yutaro Miyazaki, Mizuki Watabe, Sho Akimoto, Tatsuya Tachikawa, Koichi Kodama, Mikio Yasutake

PII: S0040-4020(15)00762-0

DOI: 10.1016/j.tet.2015.05.071

Reference: TET 26789

To appear in: Tetrahedron

Received Date: 13 April 2015

Revised Date: 19 May 2015

Accepted Date: 20 May 2015

Please cite this article as: Hirose T, Miyazaki Y, Watabe M, Akimoto S, Tachikawa T, Kodama K, Yasutake M, Trialkylsilylethynyl-substituted triphenylenes and hexabenzocoronenes: highly soluble liquid crystalline materials and their hole transport abilities, *Tetrahedron* (2015), doi: 10.1016/j.tet.2015.05.071.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



# **Graphical Abstract**

To create your abstract, type over the instructions in the template box below. Fonts or abstract dimensions should not be changed or altered.



# Trialkylsilylethynyl-substituted triphenylenes and hexabenzocoronenes: highly soluble liquid crystalline materials and their hole transport abilities

Takuji Hirose,<sup>a,\*</sup> Yutaro Miyazaki,<sup>a</sup> Mizuki Watabe,<sup>a</sup> Sho Akimoto,<sup>a</sup> Tatsuya Tachikawa,<sup>a</sup> Koichi Kodama,<sup>a</sup> and Mikio Yasutake<sup>b</sup>

<sup>a</sup> Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan.

<sup>b</sup> Comprehensive Analysis Center for Science, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan.

Corresponding author. E-mail address: thirose@mail.saitama-u.ac.jp (T. Hirose).

Keywords: trialkylsilylethynyl group, triphenylene, hexa-*peri*-hexabenzocoronene, liquid crystal, hole transport ability

# ABSTRACT

Four triphenylene (TP) and four hexa-*peri*-hexabenzocoronene (HBC) derivatives with trialkylsilylethynyl groups were prepared and characterized by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction measurements. All compounds were highly soluble in less-polar organic solvents and exhibited a columnar phase, Col<sub>h</sub> or Col<sub>r</sub> for the TPs, and Col<sub>h</sub> for the HBCs. The hole transport ability in the HBCs' columnar phase,  $0.4-1.5 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 40–180 °C, and its temperature dependence were determined by the time-of-flight method using a solution technique.

#### 1. Introduction

The development of new organic semiconductors is currently a challenging project,<sup>1</sup> and interest in liquid crystals (LCs) has grown significantly for application to electronic devices such as solar cells, organic light-emitting diodes, and organic field-effect transistors.<sup>2</sup> Semiconducting organic molecules and materials, including liquid crystalline ones, cannot yet compete with their inorganic counterparts in terms of charge transport ability and industrial performance. However, they have important advantages: versatile synthetic processes, lower production costs, and compatibility with other materials such as flexible polymeric films and inorganic substrates.

To increase the charge transport ability of LCs, aromatic structures are expected to be a key factor in improving the performance owing to their high  $\pi$ -electron density. For a columnar LC phase, the introduction of a highly symmetric polyaromatic hydrocarbon structure is typically an important strategy and leads to high one-dimensional charge transport like that through a wire. However, at the same time, it is generally recognized that the LC transition temperature rises and the solubility decreases as the fused aromatic core size is enlarged.<sup>3</sup> As a result, low solubility hinders the processability, detailed study, and even efficient syntheses.

We have synthesized and studied several types of discotic liquid crystals, including their conductive properties.<sup>4</sup> During this work, we have used pyrene as a core structure to lower the crystalline–LC phase transition temperature and improve the solubility. In the previous work, we have shown that the introduction of trialkylsilyl groups in a conjugated system is effective not only to raise the conductivity but also to increase the solubility in common organic solvents.<sup>4c</sup> If it is applicable to other systems, large and highly symmetric aromatic structures can be introduced into LCs, and high charge transport ability is expected owing to their larger  $\pi$ - $\pi$  interaction or overlap. In this study, eight new discotic liquid crystals were synthesized using triphenylene (TP), a typical core of columnar LC compounds, and hexa-*peri* hexabenzocoronene (HBC), one of the largest aromatics, having trialkylsilyl groups as a terminal of the side chains, and their chemical and physical properties, including the hole transport ability, were investigated.

# 2. Results and discussion

# 2.1. Design and Syntheses of Triphenylene [TPSi(m,n)] and Hexa-perr-hexabenzocoronene [HBCSi(m)] Derivatives

Four TP derivatives, **TPSi**(m,n) (m = 8, 9, 10; n = 1, 8, 9, 10) and four hexa-*peri* hexabenzocoronene derivatives, **HBCSi**(m) (m = 10, 12, 14, and 16), were designed by attaching trialkylsilylethynyl groups at each periphery. For **TPSi**(m,n), to enlarge the  $\pi$ -conjugation, a phenylethynyl moiety was introduced between the TP core and the terminal group. On the other hand, six trialkylsilylethynyl groups were directly attached to the HBC core. The final steps of **TPSi**(m,n) and **HBCSi**(m) syntheses are shown in

Scheme 1.

TP derivatives **TPSi**(*m,n*) were prepared from hexabromotriphenylene, **1**, as a core component and an excess amount of trialkylsilylethynylphenylacetylene, 2(m,n), as a side chain component by the Sonogashira coupling reaction. Similarly, **HBCSi**(*m*) were prepared from hexa-*peri*-hexaiodohexabenzocoronene, **3**, and alkyldimethylsilylacetylene, 4(m). In our previous work,<sup>4c</sup> the coupling reaction was performed between the core with ethynyl groups and an arylbromide as the side chain unit, and the low yield was attributed mainly to self-coupling of the core. As a result of a modification in the present study, the yields in the final Sonogashira reaction were greatly improved. (See Scheme S1 and the Synthetic Experimental section in the Supporting information for details.)



Scheme 1. Syntheses of triphenylene derivatives, **TPSi**(*m,n*), and hexa-*peri*-hexabenzocoronene derivatives, **HBCSi**(*m*). THF: Tetrahydrofuran.

# 2.2. Properties of TPSi(m,n)

## 2.2.1. Solubility

The solubility of **TPSi**(10,1) was examined for various polar and less-polar solvents. It was found that this compound dissolves well in hexane, chloroform, dichloromethane, diethyl ether, tetrahydrofuran, toluene, and chlorobenzene, like the pyrene derivatives reported previously.<sup>4c</sup> In ethyl acetate, it did not dissolve at room temperature but dissolved at a higher temperature of ~50 °C (Figure S1). On the other hand, in polar solvents such as acetone, methanol, and water, it did not dissolve at all, even at higher temperatures.

Almost the same solution behavior was observed for **TPSi**(m,m) (m = 8, 9, and 10). As a result, we did not face the solubility problem in the synthesis of **TPSi**(m,n).

#### 2.2.2. Thermal Properties

The thermal properties of **TPSi**(10,1) were studied by differential scanning calorimetry (DSC) between 0 and 200 °C. However, no phase transition was observed in this temperature range.

The thermal behaviors of **TPSi**(m,m) (m = 8, 9, and 10) were also measured by DSC and polarized optical microscopy (POM). All of them showed two transitions during both the heating and cooling processes. At the lower transition temperature, the DSC curve showed a baseline change suggesting a glass transition. At the higher transition temperature, on the other hand, the enthalpy change was rather small, ~5 kJ mol<sup>-1</sup>. The POM observation after the latter transition showed a change from the dark field to the fern texture, as shown in Figure 1a and 1b for **TPSi**(m,m) (m = 8 and 10) [Figure S2 for **TPSi**(9,9)]. The texture resembles that of pyrene derivatives bearing trialkylsilylethynyl groups<sup>4c</sup> and was easily crushed by pressing at this temperature. As this phase loses fluidity with decreasing temperature, it was expected to be an LC phase and was subjected to X-ray diffraction (XRD) measurements.



d) **HBCS**i(12) at 150 °C.

#### 2.2.3. Mesomorphism and Liquid Crystalline Structures

To determine the structure of **TPS**i(10,1), the XRD was measured at 180 °C, as shown in Figure 2a. The XRD pattern has one broad peak at  $2\theta = \sim 18^{\circ}$  and four sharp peaks at 2.84, 4.88, 5.60, and 7.48°. The peaks in the small-angle region represent the two-dimensional periodic structure of 31.1, 18.1, 15.8, and 11.8 Å, respectively, and the ratio is  $1.1/\sqrt{3.1/2.1/\sqrt{7}}$ , which corresponds well to a hexagonal lattice. Therefore, the LC phase was assigned to a disordered hexagonal columnar (Col<sub>h</sub>) phase.

To confirm this assignment, the molecular number in the unit cell *Z* was calculated using the following equation for  $\text{Col}_{h,5}$  where *a* is the lattice constant, *h* is the inter-disc distance in a column,  $\rho$  is the density,  $N_A$  is the Avogadro constant, and *M* is the molecular weight (2163.64 g mol<sup>-1</sup>).

$$Z = \frac{\sqrt{3} \cdot a^2 \cdot h \cdot \rho \cdot N_A}{2 \cdot M}$$

Assuming *h* and  $\rho$  were 3.5 Å and 1.0 g cm<sup>-3</sup>, respectively, *Z* was determined to be 1.1, indicating that the assignment is reasonable because it is close to 1.0.

In the same way, the XRD of **TPSi**(*m*,*m*) (*m* = 8, 9, and 10) was measured, and the result for **TPSi**(8,8) at 100 °C is shown in Figure 2b [see Figures S3 and S4 for **TPSi**(9,9) and **TPSi**(10, 10)]. The sharp peaks in the small-angle region (32.5, 29.6, 14.8, and 9.88 Å) and a broad one in the wide-angle region (4.7 Å) were similar to those of **TPSi**(10, 1), and the lattice was assigned to  $\text{Col}_r(\text{C2/m})$ , as the unit constants (*a*,*b*) are (59.3, 38.8). This result was also confirmed by calculating the molecular number *Z* = 2.0 in the unit cell of  $\text{Col}_r(\text{C2/m})$  using the following equation, assuming *h* = 3.7 Å and  $\rho = 1.0$  g cm<sup>-3</sup>.

$$Z = \frac{a \cdot b \cdot h \cdot \rho \cdot N_A}{M}$$

Similarly, XRD analysis was conducted for **TPSi**(m,m) (m = 9 and 10), and the lattice was determined to be Col<sub>r</sub>(C2/m) for both, with unit constants (a,b) of (62.7, 40.0) and (63.9, 41.0), respectively.

Commoniad	Phase transition temperature (°C) and enthalpy $(kJ mol^{-1})^{a,b}$			
Compound	Heating	Cooling		
<b>TPSi</b> (10,1) $0 < Col_h < 200$		$200 > Col_h > 0$		
<b>TPSi</b> (8,8)	G -85.1 Col <sub>r</sub> 209.5 (5.9) I	I 189.9 (4.6) Col <sub>r</sub> -56.7 G		
<b>TPSi</b> (9,9)	G -82.1 Col <sub>r</sub> 167.0 (5.2) I	I 159.6 (5.3) $Col_r$ -57.0 G		
<b>TPSi</b> (10,10)	G -79.2 Col <sub>r</sub> 143.9 (5.3) I	I 135.8 (4.7) Colr -60.3 G		
<b>HBCSi</b> (10)	Cr 9.3 (9.5) Colh	Col <sub>h</sub> 3.9 (9.6) Cr		
<b>HBCSi</b> (12)	$Cr_1$ [-10.2 $Cr_2$ 30.2] <sup>c</sup> (34.4) Colh	${ m Col_h}  [25.1 { m Cr}_3  \hbox{-} 9.8 { m Cr}_4  \hbox{-} 14.9 { m Cr}_5  \hbox{-} 19.2]^c \ (34.0) { m Cr}_6$		
<b>HBCSi</b> (14)	$ m Cr_1 \ [4.4 \ Cr_2 \ 40.7]^{\it c} \ (43.4) \ Col_h$	$\operatorname{Col_h}[36.4\ \operatorname{Cr}_3 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$		
<b>HBCSi</b> (16)	$Cr_1 [17.2 Cr_2 40.1]^c (57.6) Col_h$	${ m Col_h} \ [35.3 \ { m Cr}_3 \ 10.2]^c \ (58.1) \ { m Cr}_4$		

Table 1. Phase Transition Behaviors of **TPSi**(m,m) (m = 8, 9, and 10).

<sup>*a*</sup>Scan rate was 5 °C min<sup>-1</sup>. <sup>*b*</sup>Type of mesophase was determined by XRD. <sup>*c*</sup>Some phase transition peaks appeared in succession. Abbreviations: G = glassy phase, Cr = crystalline phase, Col<sub>r</sub> = rectangular columnar phase, Col<sub>h</sub> = hexagonal columnar phase, I = isotropic phase.

The thermal behaviors determined by the analysis are summarized in Table 1, and the detailed XRD data are shown in Table S1 together with those of **TPSi**(10,1). It is interesting that **TPSi**(10,1), with a less sterically hindered silyl group, forms a Col<sub>h</sub> phase. On the other hand, **TPSi**(*m*,*m*) (*m* = 8, 9, and 10), with a silyl group bearing two long alkyl chains, forms a Col<sub>r</sub> phase and changes to a glassy state at a low temperature of ~80 °C. For comparison, **TPSi**(1,1) was prepared and its single crystal structure was



Figure 2. X-ray diffraction patterns of a) **TPSi**(10,1) at 180 °C, b) **TPSi**(8,8) at 100 °C, and c) **HBCSi**(10) at 100 °C.

analyzed, as shown in Figure 3 and Table S2. The tilted molecules appeared in staggered piles, and the distance between the adjacent molecules was 3.4-3.5 Å. The structural features seem to support the determination that the structure of liquid crystalline **TPSi**(*m*,*m*) (*m* = 8, 9, and 10) exhibits a Colr phase.



Figure 3. Crystal structure of **TPSi**(1,1) with acetone. a) Top view. b) Side view.

## 2.3. Properties of HBCSi(m)

#### 2.3.1. Solubility

The solubility of **HBCSi**(*m*) (m = 10, 12, 14, and 16) in various solvents was also examined. It was found that they dissolve well in less-polar solvents, that is, in hexane, chloroform, dichloromethane, diethyl ether, tetrahydrofuran, toluene, chlorobenzene, and warm ethyl acetate (~50 °C), but not in acetone, methanol, and water, just like **TPSi**(m,n) (Figure S1).

The melting point of HBC exceeds than 700 °C, and it hardly dissolves in any common organic solvent because of a very large fused aromatic ring.<sup>6</sup> It has been shown that the introduction of linear alkyl groups generally increases its solubility, but hexa-*n*-dodecyl-hexa-*peri*-hexabenzocoronene, for example, scarcely dissolves in *n*-heptane at room temperature<sup>7</sup> and precipitates from a 1.1 wt% solution of *p*-xylene.<sup>8</sup> The present results prove that a trialkylsilyl group with one long alkyl chain effectively works

to solubilize HBC derivatives in a non-polar solvent such as hexane. It seems that the bulky trialkylsilyl groups contribute not only to increasing the mobility of the side groups but also to reducing intermolecular  $\pi$ - $\pi$  interactions.

#### 2.3.2. Intermolecular Interaction

It has been reported that HBC derivatives aggregate in solution, and the self-association is affected by not only the solvent and concentration but also the side chain structure.<sup>7a</sup> In this study, on the other hand, another interesting behavior was observed in the <sup>1</sup>H NMR spectra of **HBCSi**(*m*) in CDCl<sub>3</sub>. The aromatic protons show three broad peaks below 20 °C and at concentrations above 10<sup>-3</sup> M, as shown in Figure 4 for **HBCSi**(16). Such temperature and concentration dependences are unknown for other HBC derivatives in solution but were observed in solid-state <sup>1</sup>H NMR by Spiess *et al.*<sup>7b</sup> They discussed how the stacking of the aromatic cores in hexa-*n*-dodecyl-hexa-*peri* hexabenzocoronene produced three different aromatic proton environments. Therefore, the present results also indicate that several molecules aggregate due to  $\pi$ - $\pi$  interaction, and bulky trialkylsilyl groups restrict the molecular rotation and/or slippage, creating three different magnetic conditions for the aromatic protons. As a result, other proton signals were also observed as broad peaks at room temperature. A similar complex <sup>1</sup>H NMR spectrum of a perylene bisimide derivative was attributed to molecular aggregation in a non-polar solvent.<sup>9</sup>

#### 2.3.3. Thermal Properties

The thermal properties of **HBCSi**(*m*) (m = 10, 12, 14, and 16) were studied using DSC and POM. A large enthalpy change was observed at ~30–60 °C for **HBCSi**(*m*) (m = 12, 14, and 16). The POM observation revealed that it was not the transition to the isotropic phase, and the compounds subsequently decomposed above 200 °C without melting.<sup>10</sup> Below the transition, the texture was hard,



Figure 4. a) Temperature and b) concentration dependence of <sup>1</sup>H NMR spectra of **HBCSi**(16) in CDCl<sub>3</sub>.

but fluidity was observed above the transition. As the textures at higher temperature (above 150 °C) are stripe-like or a pseudo-focal conic, as seen in Figure 1d for **HBCSi**(12) [Figures S1b and S1c for **HBCSi**(14) and **HBCSi**(16)], the Cr–LC phase transition is suggested. Below the transition temperature, minor transitions were detected for **HBCSi**(m) (m = 12, 14, and 16) by DSC but not observed by POM measurement. At present, they are assigned as Cr–Cr transitions.

The texture of **HBCSi**(10) is also unclear, as seen in Figure 1c. However, a transition with a small enthalpy occurred at ~10 °C, and the compound was mobile after the transition. From the similar phase transition behavior, therefore, it is also expected to be the Cr–LC phase transition. As a result, in contrast to **TPSi**(m,m), the phase transition temperature of **HBCSi**(m) (m = 10, 12, 14, and 16) rose as the length of the side chain increased. However, it was difficult to identify the LC structure from the POM observation. To determine the structure at higher temperatures, all the compounds were studied by XRD, and the results are summarized in Table 1.

#### 2.3.4. Mesomorphism and Liquid Crystalline Structures

The XRD pattern for **HBCSi**(10) at 100 °C is shown in Figure 2c. [See Figures S5–S7 for **HBCSi**(*m*) (m = 12, 14, and 16).] Two broad peaks and seven sharp peaks were obtained in the wide- and small-angle regions, respectively. The spacing ratio of the sharp peaks was  $1:1/\sqrt{3}:1/2:1/\sqrt{7}:1/3:1/4:1/6}$ , which corresponds to the Colh phase. The diffraction pattern was the same for all **HBCSi**(*m*) and also for TPSi(10,1), as expected from the structure of the trialkylsilyl group (Table S3). The broad peaks at  $2\theta \ge 25^{\circ}$  were expected to represent the core stacking distances of 3.5–3.6 Å, but the regularity seemed low.

The obtained *a* values increased with increasing alkoxy carbon number *m*. The results are summarized in Table S3 for HBCSi(*m*) (m = 10, 12, 14, and 16). Consequently, it was concluded that all the phase transitions of HBCSi(*m*) are Cr–Col<sub>h</sub> phase transition. The thermal behaviors of HBCSi(*m*) (m = 12, 14, and 16) (Table 1) are close to each other and resemble those of some HBC derivatives with long alkyl side chains.<sup>3a,17</sup>

The Cr–LC transition temperature increases slightly with increasing length of the alkyldimethylsilyl group, suggesting the effect of the van der Waals interaction.<sup>3,17</sup> It was also shown that all the **HBCS**i(*m*) compounds are LCs in a wide temperature range of more than 150 K. These thermal properties are similar to those of other hexa-substituted HBCs: the Col<sub>h</sub> phase transition occurs at 60 °C for hexadodecyl HBC (a = 29.1 Å, h = 3.55 Å) and 65 °C for hexakis(hexadecyl) HBC (a = 30.7 Å, h = 3.72 Å at room temperature).<sup>7c</sup> Considering that their *h* values are quite similar to those of **HBCS**i(*m*), the trialkylsilyl groups have little effect on the molecular stacking. The trialkylsilyl groups probably fit between the side chains of adjacent disks in the LC state, and the bulkiness is eased.

#### 2.4. Charge Transport Ability of TPSi(*m*,*n*) and HBCSi(12)

The charge transport ability was studied using the time-of flight (TOF) method. To prepare the measurement cell, **TPSi**(*m*,*m*) (m = 8, 9, and 10) were melted and poured into an indium tin oxide cell (gap of 5 µm). However, **TPSi**(10,1) and **HBCSi**(12) decomposed when they were heated for melting. To fill the cell, their concentrated solutions (>100 g L<sup>-1</sup>) in hexane were injected into the cell, and the solvent was allowed to evaporate for two days. To remove the hexane completely, the cells were dried at elevated temperature under reduced pressure. After preparation, the Col<sub>h</sub> textures in the cell were confirmed by POM observation, which indicated homeotropic alignment to the electrode glass, as shown in Figure 5 for **HBCSi**(12).



Figure 5. POM texture of the sample cell of **HBCSi**(12). a) open nicol, b) crossed nicols.

The hole transport abilities  $\mu_h$  of **TPSi**(m,n) (m = 10, n = 1; m = n = 8, 9, 10) were measured. However, the photocurrents were dispersive, so the TOF could not be determined. The disordered stacking of molecules is thought to prevent smooth charge transport, as suggested by the lack of clear diffraction in the wide-angle region for all **TPSi**(m,n).

On the other hand, for **HBCSi**(12) at 140 °C, a clear inflection was obtained in the double logarithmic plot of the photocurrent, as shown in Figure 6. It is known that the charge transport in the LC phase does not depend on the electric field strength, *E*, because there is no trap near the phase boundary. For **HBCSi**(12), the dependence was examined at 12–20 kV cm<sup>-1</sup>, and the hole mobility was confirmed to be constant (Figure S8), showing a value of  $1.55 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 140 °C (Figure 6).

The temperature dependence was also examined at 40–180 °C for **HBCSi**(12). As shown in Figure 7, the hole mobility increased up to 100 °C but became constant above 120 °C, and no electric field dependence was observed at any temperature. In addition, little difference was observed between the heating and cooling processes at 100 and 180 °C. These results also indicate that **HBCSi**(12) is in the LC phase. Funahashi and Sonoda discussed the relationship between the temperature dependence of the charge mobility and the stacking distance.<sup>11</sup> However, in this study, it was difficult to discuss this relationship because precise measurement of the stacking distance was difficult owing to the broad diffraction peak.



Figure 6. Typical transient photocurrents in Col<sub>h</sub> phase of **HBCSi**(12) at 140 °C under several applied biases for positive charge carriers. Inset shows the double logarithmic plots. Sample thickness was  $5 \mu m$ .



Figure 7. Temperature dependence of the hole mobilities in the Col<sub>h</sub> phase of **HBCSi**(12) during the heating ( $\triangle$ ) and cooling ( $\bigcirc$ ) processes. Sample thickness was 5 µm.

From the Arrhenius plot of the hole mobility below 100 °C, an activation energy of 0.18 eV was calculated. It is reported that the activation energy of ionic charge transport is ~0.3 eV, and that of charge hopping between molecules is expected to be much lower than this value.<sup>12,13</sup> Therefore, the present result supports hole transport but not ion transport.

A non-dispersive photocurrent was obtained for **HBCSi**(12) owing to the molecular packing in the columnar structure. The value was as much as that of hexa(2-hexyldecyl) HBC<sup>14</sup> and

hexaalkyltriphenylene in the Col<sub>h</sub> phase<sup>13a,15</sup> obtained by TOF but about 2 orders of magnitude lower than those reported for HBC derivatives obtained using the pulse radiolysis time-resolved microwave conductivity.<sup>3a</sup> Considering the <sup>1</sup>H NMR (Figure 4) in solution, the strong  $\pi$ - $\pi$  interaction and bulky side chain seem the main reasons; that is, the random aggregation of molecules in the LC state caused the disordered packing of the aromatic rings, and the bulky side chain staggered the aromatic rings, which produced the broad XRD peaks.

#### 2.5. Spectroscopic and Redox Properties of HBCSi(m)

The spectroscopic properties of **TPSi**(9,9) and **HBCSi**(*m*) (m = 12 and 14) were measured in CH<sub>2</sub>Cl<sub>2</sub>; the UV-vis and emission spectra of **HBCSi**(12) are summarized in Figure 8. The UV-vis and emission spectra have similar features to those reported previously.<sup>10,16</sup> However, the absorption spectrum is red-shifted compared to that of simply alkyl- or alkoxy-substituted ones<sup>16a,16b</sup> and that of **TPSi**(9,9) (Figure S9), like those of larger  $\pi$ -conjugated molecules. Although the emission spectrum displays no structure, the highest occupied molecular orbital-lowest unoccupied molecular orbital energy gap is close to the reported values.<sup>16c,16d</sup> Almost the same spectra were obtained for **HBCSi**(14) (Figure S10).

All the absorption and emission maxima and the optical band gaps ( $\Delta E_{opt}$ ) are summarized in Table 2. The similarities between the present data and the literature values<sup>16</sup> do not seem to correspond to the charge transport properties of **HBCSi**(12) and hexadodecyl HBC.<sup>3a</sup> The results demonstrate that the molecular properties do not necessarily lead to the bulk properties such as charge transport ability, and a more elaborate LC molecule design is necessary for use a bulk material as well as a molecular device.



Figure 8. (a) UV–vis and (b) emission spectra of **HBCSi**(12) ( $\lambda_{ex}$ : 380 nm). In dry CH<sub>2</sub>Cl<sub>2</sub>, 1 × 10<sup>-6</sup> M.

- I		,-,		
Compound	λ <sub>max</sub> (nm)	<mark>λ<sub>em</sub> (nm)</mark>	$\Delta E_{\rm opt}^{b} (eV)$	
<b>TPSi</b> (9,9)	<mark>363</mark>	<mark>433</mark>	<mark>3.14</mark>	
<b>HBCSi</b> (12)	378	521	3.08	
<b>HBCSi</b> (14)	378	519	3.08	
$a1.0 \times 10^{-7}$ M for	r <b>TPSi</b> (9.9) g	and $1.0 \times 10$	-6 M for HRC	Si(n

Table 2. Spectroscopic Data of **TPSi**(9,9) and **HBCSi**(m) (m = 12 and 14).<sup>*a*</sup>

 $^{a}1.0 \times 10^{-7}$  M for **TPSi**(9,9) and  $1.0 \times 10^{-6}$  M for **HBCSi**(*m* (*m*=12 and 14) in deaerated CH<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup>Optical band gap calculated from the onset of the absorption band.

#### 3. Conclusion

Two types of discotic liquid crystals were designed and prepared using TP and hexa-peri-hexabenzocoronene as the large aromatic core structures. The introduction of a trialkylsilylethynyl group with one or two long alkyl groups was shown to be effective to increase the solubility in common organic solvents. Their thermal behaviors and mesomorphism were studied in detail. The TP derivatives **TPSi**(m,m) (m = 8, 9, and 10) showed the Col<sub>r</sub> phase, whereas **TPSi**(10,1) and **HBCSi**(*m*) (m = 10, 12, 14, and 16) showed the Col<sub>h</sub> phase. All the TP derivatives **TPSi**(*m*,*n*) did not show any charge mobility, probably because the molecular stacking was disordered and unsuitable for the present measurement. On the other hand, **HBCSi**(12) showed a hole mobility of  $\sim 1.5 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 140 °C, which is 2 orders of magnitude lower than that reported for hexa-peri-hexabenzocoronene derivatives. The bulky side chains and strong  $\pi$ -stacking seemed to be the reasons for the lower charge mobility. New designs of highly soluble HBC liquid crystals are in progress.

14

#### 4. Experimental section

#### 4.1. General

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker DRX-400 spectrometer [Comprehensive Analysis Center for Science (CACS), Saitama University]. The chemical shift was reported in parts per million using tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-460 spectrometer. UV–vis and emission spectra of all the compounds were recorded in a dichloromethane solution on a JASCO V-550 instrument.

Cyclic voltammetry was performed using an ALS CHI 611D electrochemical analyzer. The measurements were conducted in dichloromethane containing a 0.1 M solution of n-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte (scan rate: 200 mV s<sup>-1</sup>) at room temperature. The concentration of  $\mathbf{1}_n$  was 1.0 × 10<sup>-3</sup> M. A glassy carbon electrode was used as the working electrode, a platinum wire was used as the counter electrode, and a Ag/AgNO<sub>3</sub> electrode was used as the reference electrode. The Ag/AgNO<sub>3</sub> reference electrode was calibrated against a ferrocene/ferrocenium redox couple.

Matrix-assisted laser desorption/ionization-time of flight mass spectra were measured with a Bruker Daltonics Autoflex III instrument (CACS). X-ray diffraction analysis was performed on a quartz substrate using a Rigaku model Ultima III X-ray diffractometer with a monochromated CuKα radiation source (wavelength of 0.1542 nm, 40 kV, 40 mA) (CACS).

Melting points were determined with a Mitamura Riken Kogyo MEL-TEMP instrument and reported uncorrected. Phase transition temperatures were determined using a Mac Science DSC-3100 differential scanning calorimeter. A Nikon OPTIPHOT2-POL optical polarized microscope equipped with a Mettler FP-82 hot stage and a Mettler FP-90 central processor was used to characterize the anisotropic textures.

All commercially available reagents and solvents were purchased from Wako Pure Chemical Inc., Kanto Chemical Inc., Tokyo Kasei Kogyo Co., and Aldrich Chemical Co., and were used as received except for dry tetrahydrofurane, dry toluene, dry dichloromethane, and dry diethylamine. The dry solvents were prepared according to the standard procedure.

#### 4.2. Synthesis

#### 4.2.1. Typical Procedure for the Synthesis of

#### 2,3,6,7,10,11-Hexakis(trialkylsilylethynylphenylethynyl)triphenylene TPSi(m,n)

2,3,6,7,10,11-Hexakis{4-[(methyldioctylsilyl)ethynyl]phenylethynyl}triphenylene TPSi(8,8)

Under nitrogen,  $PdCl_2(PPh_3)_2$  (28.7 mg, 40.8 µmol),  $PPh_3$  (21.1 mg, 80.3 µmol), **6**(8,8) (654 mg, 1.67 mmol),  ${}^{7}Pr_2NH$  (10 mL), and CuI (7.58 mg, 39.8 µmol) were added to **1** (140 mg, 200 µmol) in dry toluene (10 mL). After stirring at 60 °C for 17 h, the reaction mixture was cooled to room temperature, and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a dark brown liquid. The residue was purified by silica gel column chromatography with hexane and

hexane/chloroform (v/v, 1/1) and by thin-layer chromatography with hexane/chloroform (v/v, 5/1) to give a yellow sticky wax-like solid (315 mg, 122 µmol, 61.0%). MS (MALDI-TOF, DHB) m/z: 2581.861 [M]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.69 (s, 6H, Ar-H), 7.57 (d, J = 8.4 Hz, 12H, Ar-H), 7.48 (d, J = 8.4 Hz, 12H, Ar-H), 1.51–1.23 (m, 144H, -C $H_2$ -), 0.89 (t, J = 6.9 Hz, 36H, -C $H_3$ ), 0.77–0.67 (m, 24H, Si-C $H_2$ -), 0.22 (s, 18H, Si-C $H_3$ ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.8, 128.6, 127.2, 124.8, 123.79, 123.1, 105.5, 95.9, 94.7, 90.3, 33.6, 32.1, 29.5, 24.1, 22.9, 14.9, 14.3, -3.2; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2922, 2853, 2155, 1510, 1466, 1410, 1250, 835; Anal. Calcd for C<sub>180</sub>H<sub>252</sub>Si<sub>6</sub>: C, 83.65%; H, 9.82%. Found: C, 83.61%; H, 9.88%.

#### Other **TPSi**(m,n) were prepared following the same procedure for **TPSi**(8,8).

2,3,6,7,10,11-Hexakis{4-[(dinonylmethylsilyl)ethynyl]phenylethynyl]triphenylene **TPSi**(9,9) Yield (47.2%: sticky wax-like solid); MS (MALDI-TOF, DHB) m/z: 2750.043 [M]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.79 (s, 6H, Ar-H), 7.58 (d, J = 8.7 Hz, 12H, Ar-H), 7.48 (d, J = 8.7 Hz, 12H, Ar-H), 1.50-1.23 (m, 168H,  $-CH_2$ -), 0.89 (t, J = 6.9 Hz, 36H,  $-CH_3$ ), 0.75-0.66 (m, 24H, Si- $CH_2$ -), 0.21 (s, 18H, Si- $CH_3$ ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.8, 128.6, 127.3, 124.9, 123.8, 123.1, 105.5, 95.9, 94.7, 90.3, 33.6, 32.1, 29.8, 29.6, 24.1, 22.9, 14.9, 14.3, -3.2; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2923, 2853, 2154, 1510, 1466, 1410, 1250, 835; Anal. Calcd for C<sub>192</sub>H<sub>276</sub>Si<sub>6</sub>: C, 83.77; H, 10.11%. Found: C, 83.73; H, 10.16%.

2,3,6,7,10,11-Hexakis{4-[(didecylmethylsilyl)ethynyl]phenylethynyl}triphenylene **TPSi**(10,10) Yield (41.7%: sticky wax-like solid); MS (MALDI-TOF, DHB) m/z: 2918.207 [M]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.59 (s, 6H, Ar-H), 7.56 (d, J = 8.4 Hz, 12H, Ar-H), 7.47 (d, J = 8.4 Hz, 12H, Ar-H), 1.52-1.22 (m, 192H, -C $H_2$ -), 0.89 (t, J = 6.6 Hz, 36H, -C $H_3$ ), 0.78-0.69 (m, 24H, Si-C $H_2$ -), 0.24 (s, 18H, Si-C $H_3$ ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.7, 128.7, 127.4, 124.9, 123.8, 123.1, 105.5, 95.9, 94.7, 90.3, 33.6, 32.1, 29.9, 29.8, 29.6, 24.1, 22.9, 14.9, 14.3, -3.3; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2922, 2853, 2149, 1465, 1418, 1249, 1003, 868, 840; Anal. calcd for C<sub>204</sub>H<sub>300</sub>Si<sub>6</sub>: C, 83.88; H, 10.35%. found: C, 83.50; H, 10.35%.

Yield (70.4%: sticky wax-like solid); MS (MALDI-TOF, DHB) m/z: 2161.352 [M]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.31 (s, 6H, Ar-H), 7.48 (d, J = 8.4 Hz, 12H, Ar-H), 7.42 (d, J = 8.4 Hz, 12H, Ar-H), 1.56-1.26 (m, 96H, -C $H_2$ -), 0.89 (t, J = 6.6 Hz, 18H, -C $H_3$ ), 0.80-0.72 (m, 12H, Si-C $H_2$ -), 0.30 (s, 36H, Si-C $H_3$ ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.8, 128.3, 127.2, 124.3, 123.6, 123.2, 105.2, 96.3, 94.6, 90.5, 33.6, 32.1, 29.9, 29.6, 24.0, 22.9, 16.4, 14.3, -1.5; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2924, 2853, 2156, 1510, 1466, 1415, 1250, 1016, 879, 835; Anal. Calcd for C<sub>150</sub>H<sub>192</sub>Si<sub>6</sub>: C, 83.27; H, 8.94%. Found: C, 82.50; H, 9.07%.

4.2.2. Typical for the of procedure synthesis 2,5,8,11,14,17-Hexakis[(trialkylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene HBCSi(m) 2,5,8,11,14,17-Hexakis[(decyldimethylsilyl)ethynyl]hexa-peri-hexabenzocoronene HBCSi(10) Under nitrogen, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (15.07 mg, 21.5 µmol), PPh<sub>3</sub> (11.12 mg, 42.4 µmol), 4(10,1) (404 mg, 1.80 mmol),  $Pr_2NH$  (4.0 mL) and CuI (5.52 mg, 29.0 µmol) were added to the solution of **3** (256 mg, 200 µmol) in dry toluene (4.0 mL). After stirring at 50 °C for 5 h, the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure to give a reddish brown liquid. The residue was washed with AcOEt several times to get an orange solid. The solid was further purified by preparative GPC (JAIGEL-1H/2H, CHCl<sub>3</sub>) to give **HBCSi**(10) an orange-yellow sticky wax-like solid (609 mg, 0.319 mmol, 52.8%). MS (MALDI-TOF, DHB) m/z (%): 1855.92 [M+H]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.95–7.70 (br, 12H, Ar-*H*), 2.00-0.74 (br, 126H, Si-CH<sub>2</sub>-, -CH<sub>2</sub>-, -CH<sub>3</sub>), 0.61 (s, 36H, Si-CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 128.60, 125.25, 123.58, 121.54, 119.77, 106.16, 95.02, 33.63, 31.90, 29.84, 29.78, 29.69, 29.59, 29.36, 24.10, 22.64, 16.55, 14.03, 0.01, -1.08; IR  $(KBr): v_{max} (cm^{-1}) = 2956, 2922, 2853, 2151, 1603, 1571, 1466, 1418, 1366, 1248, 1164, 1004, 869, 841, 1004, 100$ 820; Anal. Calcd for C<sub>126</sub>H<sub>174</sub>Si<sub>6</sub>: C, 81.48; H, 9.44%. Found: C, 81.46; H, 9.46%.

#### Other HBCSi(m) were prepared following the same procedure for HBCSi(10).

2,5,8,11,14,17-Hexakis[(dodecyldimethylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(12) Yield (58.8%: sticky wax-like solid); MS (MALDI-TOF, DHB) m/z: 2024.18 [M+H]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.95-7.70 (br, 12H, Ar-H), 2.15-0.74 (br, 150H, Si-C $H_2$ -, -C $H_2$ -, -C $H_3$ ), 0.61 (br, 36H, Si-C $H_3$ ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 128.54, 125.18, 123.24, 121.49, 119.75, 106.17, 95.04, 33.65, 31.90, 29.84, 29.78, 29.69, 29.60, 29.37, 24.12, 22.64, 16.56, 14.03, 0.01, -1.08; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2922, 2852, 2151, 1604, 1466, 1366, 1248, 1004, 868, 840; Anal. Calcd for C<sub>138</sub>H<sub>198</sub>Si<sub>6</sub>: C, 81.83; H, 9.85%. Found: C, 81.33; H, 10.10%.

2,5,8,11,14,17-Hexakis[(dimethyltetradecylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(14) Yield (45.6%: sticky wax-like solid); MS (MALDI-TOF, DHB) *m/z* (%): 2192.36 [M+H]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.90-7.75 (br, 12H, Ar-H), 2.05-0.72 (br, 174H, Si-C*H*<sub>2</sub>-, -C*H*<sub>2</sub>-, -C*H*<sub>3</sub>), 0.60 (br, 36H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 128.62, 128.17, 127.20, 125.28, 124.94, 123.53, 123.05, 121.61, 121.13, 120.64, 119.78, 119.03, 117.86, 106.15, 95.15, 94.79, 33.60, 31.87, 29.78, 29.74, 29.64, 29.33, 24.08, 22.62, 16.54, 14.03, 0.01, -1.07; IR (KBr): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2955, 2922, 2852, 2151, 1604, 1572, 1467, 1418, 1366, 1248, 1165, 1004, 869, 841; Anal. Calcd for C<sub>150</sub>H<sub>222</sub>Si<sub>6</sub>: C, 82.12; H, 10.20%. Found: C, 82.26; H, 10.26%.

2,5,8,11,14,17-Hexakis[(hexadecyldimethylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(16) Yield (42.9%: sticky wax-like solid); MS (MALDI-TOF, DHB) *m/z*: 2360.44 [M+H]+; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.95-7.80 (br, 12H, Ar-H), 2.00-0.90 (br, 186H, -C*H*<sub>2</sub>-), 0.79 (t, *J* = 6.9 Hz, 12H, Si-C*H*<sub>2</sub>-),

0.61 (s, 36H, Si-C $H_3$ ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 128.58, 125.28, 123.44, 121.52, 119.81, 106.17, 95.07, 33.60, 31.86, 29.84, 29.78, 29.72, 29.68, 29.60, 29.30, 24.12, 22.62, 16.55, 14.05, 0.01, -1.10; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.66 (br, 12H, Ar-H), 1.78-0.95 (m, 168H, -C $H_2$ -), 0.79 (t, J = 6.9 Hz, 18H, -C $H_3$ ), 0.61 (br, 36H, Si-C $H_3$ ); IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2922, 2852, 2150, 1603, 1468, 1366, 1248, 1004, 868, 830; Anal. Calcd for C<sub>162</sub>H<sub>246</sub>Si<sub>6</sub>: C, 82.37; H, 10.50%. Found: C, 82.35; H, 10.61%.

#### References

 (a) Organic Electronics: Materials, Manufacturing, and Applications; Klauk, H. Ed; Wiley-VCH: Weinheim, 2006; (b) Anthony, J. E. Angew. Chem. Int. Ed., 2008, 47, 452–483.

2. (a) Liquid Crystalline Semiconductors; Bushby, R. J.; Kelly, S. M.; O'Neil, M. Eds; Springer: Dordrecht,
2012; b) Simpson, C. D.; Wu, J.; Watson, M. D.; Müllen, K. J. Mater. Chem., 2004, 14, 494–504; c)
Funahashi, M. Polym. J., 2009, 41, 459–469.

3. (a) van de Craats, A. M.; Warman, J. M.; Fechtenkötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. Adv. Mater., 1999, 11, 1469–1472; (b) Fechtenkötter, A.; Saalwächter, K.; Harbison, M. A.; Müllen, K.; Spiess, H. W. Angew. Chem. Int. Ed. Engl., 1999, 38, 3039–3042.

4. (a) Yasutake, M.; Fujiwara, T.; Nagasawa, A.; Moriya, K.: Hirose, T.: *Euro. J. Org. Chem.*, 2008, 4120–4125; (b) Hirose, T.; Yumoto, T.; Matsumoto, K.; Mitsushio, S.; Kawakami, O.; Yasutake, M. *Mol. Cryst. Liq. Cryst.* 2010, *524*, 68–101; (c) Hirose, T.; Shibano, Y.; Miyazaki, Y.; Sogoshi, N.; Nakabayashi, S.; Yasutake, M. *Mol. Cryst. Liq. Cryst.*, 2011, *534*, 81–92; (d) Hirose, T.; Takai, H.; Watabe, M.; Minamikawa, H.; Tachikawa, T.; Kodama, K.; Yasutake, M. *Tetrahedron*, 2014, *70*, 5100–5108.

5. Ohta, K. *Dimensionality and Hierarchy of Liquid Crystalline Phases: X-ray Structural Analysis of the Dimensional Assemblies*; Shinshu University Institutional Repository, **2013**; http://hdl.handle.net/10091/17016.

 Beginn, C.; Grazulevicius, J. V.; Strohriegl, P.; Simmerer, J.; Haarer, D. Macromol. Chem. Phys., 1994, 195, 2353–2370.

7. (a) Kastler, M.; Pisula, W.; Wasserfallen, D; Pakula, T.; Müllen, K. J. Am. Chem. Soc. 2005, 127, 4286–4296; b) Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. J. Am. Chem. Soc. 1999, 121, 6712–1618; c) Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. Adv. Mater. 1996, 8, 510–513; d) Stabel, A.; Herwig, P.; Müllen, K.; Rabe, J. P. Angew. Chem. Int. Ed. 1995, 34,1609–1611.

8. Kim, H.-S.; Lee, J.-H.; Kim, T.-H.; Okabe, S.; Shibayama, M.; Choi, S.-M. *J. Phys. Chem.*, **2011**, *115*, 7314–7320.

9. Chen, Z.; Stepanenko, V.; Dehm, V.; Prins, P.; Siebbeles, L. D. A.; Seibt, J.; Marquetand, P.; Engel, V.; Würthner, F. *Chem. Eur. J.*, **2007**, *13*, 436–449.

10. Wu, J.; Watson, M. D.; Zhang, L.; Wang, Z.; Müllen, K. J. Am. Chem. Soc., 2004, 126, 177-186.

11. Funahashi, M.; Sonoda, A. J. Mater. Chem., 2012, 22, 25190-25197.

12. (a) Sienkowska, M. J.; Monobe, H.; Kaszynski, P.; Shimizu, Y. J. Mater. Chem., 2007, 17, 1392–1398;
(b) Kreouzis, T.; Donovan, K. J.; Boden, N.; Bushby, R. J.; Lozman, O. R.; Liu, Q. J. Chem. Phys., 2001, 114, 1797–1802; (c) Nakayama, H.; Ozaki, M.; Schmidt, W. F.; Yoshino, K. Jpn. J. Appl. Phys., 1999, 38, L1038–L1041.

13. (a) Iino, H.; Hanna, J.; Jäger, C.; Haarer, D. *Mol. Cryat. Liq. Cryst.*, **2005**, *436*, 217–224; (b) Iino, H.; Hanna, J.; Haarer, D.; Bushby, R. J. *Jpn. J. Appl. Phys.*, **2006**, *45*, 430–433.

14. Kastler, M.; Laquai, F.; Müllen, K.; Wegner, G. Appl. Phys. Lett., 2006, 89, 252103.

15. Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbachi, K.

H.; Ringsdorf, H.; Haarer, D. Nature, 1994, 371, 141-143.

16. (a) Wang, Z.; Watson, M. D.; Wu, J.; Müllen, K. *Chem. Commun.*, 2004, 336–337; (b) Murphy, F. A.; Draper, S. M. J. Org. Chem., 2010, 75, 1862–1870; (c) Wong, W. W. H.; Khoury, T.; Vak, D.; Yan, C.; Jones, D. J.; Crossley, M. J.; Holmes, A. B. J. Mater. Chem., 2010, 20, 7005–7014; (d) Roberts, D. J.; Nolan, D.; Ó Máille, G. M.; Watson, G. W.; Singh, A.; Ledoux-Rak, I.; Draper, S. M. Dalton Trans., 2012, 41, 8850–8860.

17. (a) Fechtenkötter, A.; Tchebotareva, N.; Watson, M.; Müllen, K. *Tetrahedron*, 2001, 57, 3769–3783;
(b) Fischbach, I.; Pakula, T.; Minkin, P.; Fechtenkötter, A.; Müllen, K.; Spiess, H. W. Saalwächter, K. J. *Phys. Chem. B*, 2006, 106, 6408–6418.

20

# **Supporting Data**

# Trialkylsilylethynyl-substituted triphenylenes and hexabenzocoronenes: Highly soluble liquid crystalline materials and hole transport abilities

Takuji Hirose,<sup>a</sup>,\* Yutaro Miyazaki,<sup>a</sup> Mizuki Watabe,<sup>a</sup> Sho Akimoto,<sup>a</sup> Tatsuya Tachikawa,<sup>a</sup> Koichi Kodama,<sup>a</sup> and Mikio Yasutake<sup>b</sup>

<sup>a</sup> Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan.

<sup>b</sup> Comprehensive Analysis Center for Science, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan.

Scheme S1	1
Table S1. X-ray diffraction data of $\textbf{TPSi}(m,n)$ (m = 8, 9, and 10; n = 1, 8, 9, and 10)	16
Table S2. Single crystal X-ray analysis data of <b>TPS</b> (1,1)	17
Table S3. X-ray diffraction data of <b>HBCSi</b> (m) (m = 8, 10, 12, 14, and 16)	18
Figure S1. Figure S1. Solubility tests of <b>TPSi</b> (10,1) and <b>HBC</b> (10)	
for various solvents	19
Figure S2. POM textures of a) <b>TPSi(9,9)</b> at 152 °C, b) <b>HBCSi</b> (14) at 150 °C,	
and c) <b>HBCSi</b> (16) at 150 °C	19
Figure S3. XRD pattern of <b>TPSi</b> (9,9) at 100 °C	20
Figure S4. XRD pattern of <b>TPSi</b> (10,10) at 100 °C	20
Figure S5. XRD pattern of <b>HBCSi</b> (12) at 100 °C	21
Figure S6. XRD pattern of <b>HBCSi</b> (14) at 100 °C	21
Figure S7. XRD pattern of <b>HBCSi</b> (16) at 100 °C	22
Figure S8. Electric field dependence of the hole mobility in $Col_h$ phase of <b>HBCSi</b> (12)	2)
at 140 °C. The sample thickness was 5 μm.	22
Figure S9. The UV-vis (a) and Emission (b) spectra of <b>TPSi</b> (9,9) (λ <sub>ex</sub> : 363 nm).	23
In dry CH <sub>2</sub> Cl <sub>2</sub> , $1 \times 10^{-7}$ M.	
Figure S10. The UV-vis (a) and Emission (b) spectra of <b>HBCSi</b> (14) ( $\lambda_{ex}$ : 380 nm).	23
In dry CH <sub>2</sub> Cl <sub>2</sub> , $1 \times 10^{-6}$ M.	









9





Br∖

Br

g





Scheme S1 Synthesis of **TPSi**(m,n) (m = 10, n = 1; m = n = 8, 9, 10) and **HBCSi**(m) (m = 10, 12, 14, 16). Reagents and conditions: (a) 1) Mg, dry THF, rt, 2) chlorodimethylsilane or dichloromethylsilane, 0 °C to rt, 3) 1 N HCl *aq.*; (b) CCl<sub>4</sub>, PdCl<sub>2</sub>, rt; (c) 1) HC=CMgCl, dry THF, 0 °C to rt, 2) 1 N HCl *aq.*; (d) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PPh<sub>3</sub>, CuI, dry THF, <sup>4</sup>Pr<sub>2</sub>NH,  $\Delta$ ; (e) NaOH, dry toluene, reflux; (f) I<sub>2</sub>, *hv*, benzene; (g) Br<sub>2</sub>, Fe, nitrobenzene, rt to 210 °C; (h) Br<sub>2</sub>, Et<sub>2</sub>O; (i) KOH, EtOH, reflux; (j) PdCl<sub>2</sub>(PhCN)<sub>2</sub>, dry CH<sub>2</sub>Cl<sub>2</sub>; (k) I<sub>2</sub>, PIFA, dry CH<sub>2</sub>Cl<sub>2</sub>; (l) FeCl<sub>3</sub>-CH<sub>3</sub>NO<sub>2</sub>, dry CH<sub>2</sub>Cl<sub>2</sub>, rt; (m) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PPh<sub>3</sub>, CuI, dry toluene, <sup>4</sup>Pr<sub>2</sub>NH, 50 °C.

1. Synthesis of Trialkylsilane **5**(m,n)



Typical procedure for the synthesis of 5(m,1) (n = 1) Decyldimethylsilane 5(10,1)

Under nitrogen, 1-bromodecane (3.98 g, 18.0 mmol) was added dropwise to Mg (492 mg, 20.2 mmol) in dry THF (20 mL) at rt over 15 min and stirred for 1 h. To the solution was added chlorodimethylsilane (1.80 mL, 16.2 mmol) dropwise at 0 °C over 10 min, warmed up to rt and stirred for 2 h. After adding 1 N HCl *aq.* to quench the reaction, the precipitate was removed by filtration and the filtrate was concentrated to remove THF. The residue was dissolved in hexane and washed with water. The organic layer was dried over *anhyd.* Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a pale yellow liquid. The crude product was distilled by Kugelrohr (< 10 mmHg, 180 °C) to afford a colorless liquid (3.15 g, 15.7 mmol, 96.9%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.83 (nonet, *J* = 3.6 Hz, 1H, Si-*H*), 1.38-1.23 (m, 16H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>), 0.62-0.56 (m, 2H, Si-C*H*<sub>2</sub>-), 0.06 (d, *J* = 3.6 Hz, 6H, -C*H*<sub>3</sub>); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 2958, 2925, 2855, 2114, 1466, 1250, 890, 836.

Other 5(m,1) were prepared following the same procedure for 5(10,1).

Dodecyldimethylsilane 5(12,1)

Yield (96.4%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.83 (nonet, J = 3.6 Hz, 1H, Si-H), 1.39-1.23 (m, 20H,  $-CH_2$ -), 0.88 (t, J = 6.9 Hz, 3H,  $-CH_3$ ), 0.62-0.53 (m, 2H, Si- $CH_2$ -), 0.06 (d, J = 3.6 Hz, 6H, Si- $CH_3$ ); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 2958, 2925, 2855, 2114, 1467, 1250, 891, 836.

Dimethyltetradecylsilane 5(14,1)

Yield (91.4%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.84 (nonet, J = 3.6 Hz, 1H, Si-H), 1.38-1.23 (m, 24H, -C $H_2$ -), 0.89 (t, J = 6.6 Hz, 3H, -C $H_3$ ), 0.62-0.53 (m, 2H, Si- $CH_2$ -), 0.03 (d, J = 3.6 Hz, 6H, Si- $CH_3$ ); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 2957, 2925, 2854, 2113, 1467, 1250, 889, 836.

#### Hexadecyldimethylsilane 5(16,1)

Yield (90.9%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.84 (nonet, J = 3.6 Hz, 1H, Si-H), 1.38-1.23 (m, 28H,  $-CH_2$ -), 0.89 (t, J = 6.6 Hz, 3H,  $-CH_3$ ), 0.61-0.55 (m, 2H, Si- $CH_2$ -), 0.04 (d, J = 3.6 Hz, 6H, Si- $CH_3$ ); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 2957, 2925, 2854, 2114, 1466, 1250, 889, 836.

Typical procedure for the synthesis of 5(m,m) (m = n) Methyldioctylsilane 5(8,8)

Under nitrogen, 1-bromooctane (10.6 g, 54.9 mmol) was added dropwise to Mg (1.46 mg, 60.1 mmol) in dry THF (60 mL) at rt over 30 min and stirred for 3 h. To the solution was added dichloromethylsilane (2.50 mL, 24.3 mmol) dropwise at 0 °C over 10 min, warmed up to room temperature and stirred for 2 h. After adding 1 N HCl *aq.* to quench the reaction, the precipitate was removed by filtration and the filtrate was concentrated to remove THF. The residue was dissolved in hexane and washed with water. The organic layer was dried over *anhyd.* Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a pale yellow liquid. The crude product was distilled by Kugelrohr (< 10 mmHg, 180 °C) to afford a colorless liquid (6.34 g, 23.4 mmol, 96.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.75 (oct, *J* = 3.6 Hz, 1H, Si-*H*), 1.38-1.23 (m, 24H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 6H, -C*H*<sub>3</sub>), 0.62-0.52 (m, 4H, Si-C*H*<sub>2</sub>-), 0.03 (d, *J* = 3.6 Hz, 3H, Si-C*H*<sub>3</sub>); IR (neat): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2958, 2924, 2854, 2106, 1466, 1251, 880, 721.

Other 5(m,m) (m = n = 9, 10) were prepared following the same procedure for 5(8,8). Methyldinonylsilane 5(9,9)

Yield (86.1%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.75 (oct, J = 3.6 Hz, 1H, Si-H), 1.39-1.23 (m, 28H, -C $H_2$ -), 0.88 (t, J = 6.9 Hz, 6H, -C $H_3$ ), 0.62-0.53 (m, 4H, Si-C $H_2$ -), 0.03 (d, J = 3.6 Hz, 3H, Si-C $H_3$ ); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 2958, 2925, 2854, 2108, 1466, 1251, 883, 721.

Didecylmethylsilane 5(10,10)

Yield (98.0%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 3.75 (oct, J = 3.6 Hz, 1H, Si-H), 1.38-1.24 (m, 32H, -C $H_2$ -), 0.88 (t, J = 6.6 Hz, 6H, -C $H_3$ ), 0.62-0.55 (m, 4H, Si-C $H_2$ -), 0.03 (d, J = 3.6 Hz, 3H, Si-C $H_3$ ); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 2958, 2925, 2854, 2107, 1467, 1253, 882, 721.

2. Synthesis of Chlorotrialkylsilane 6(m,n)<sup>[23]</sup>



Typical procedure for the synthesis of 6(m,1)Chlorodecyldimethylsilane 6(10,1)

Under nitrogen,  $PdCl_2$  (23.3 mg, 0.131 mmol) was added to **5**(10,1) (2.41 g, 12.0 mmol) in dry  $CCl_4$  (20.0 mL, 206 mmol) and stirred for 2 h. The solvent was removed under reduced pressure to give a colorless liquid with Pd precipitate. Purification of the crude product by Kugelrohr distillation apparatus (< 10 mmHg, 180 °C) afforded a colorless liquid (2.33 g, 9.93 mmol, 82.8%).

Other **6**(m,n) were prepared following the same procedure for **6**(10,1). Chlorododecyldimethylsilane **6**(12,1) Yield (89.1%)

Chlorodimethyltetradecylsilane **6**(14,1) Yield (90.0%)

Chlorohexadecyldimethylsilane **6**(16,1) Yield (86.7%)

Chloromethyldioctylsilane **6**(8,8) Yield (88.0%)

Chloromethyldinonylsilane **6**(9,9) Yield (85.9%)

Chlorodidecylmethylsilane **6**(10,10) Yield (92.0%)

3. Synthesis of Trialkylsilylacetylene 4(m,n)



Typical procedure for the synthesis of 4(m,n)Decyldimethylsilylacetylene 4(10,1)

Under nitrogen, **6**(10,1) (2.33 g, 9.93 mmol) was added dropwise to ethynylmagnesium chloride (12.5 mmol) in dry THF (40 mL) at 0 °C over 20 min and stirred until the solution was warmed to room temperature. After adding 1 N HCl *aq.*, THF was removed under reduced pressure. The residue was dissolved in hexane and washed with 1 N HCl *aq.* and water. The organic layer was dried over *anhyd.* Na<sub>2</sub>SO<sub>4</sub>. Purification of the crude product by Kugelrohr distillation apparatus (< 10 mmHg, 180 °C) afforded a colorless liquid (1.84 g, 8.20 mmol, 82.6%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.35 (s, 1H, -C*H*), 1.44-1.25 (m, 16H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 3H, -C*H*<sub>3</sub>), 0.67-0.58 (m, 2H, Si-C*H*<sub>2</sub>-), 0.16 (s, 6H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 3295, 2959, 2925, 2855, 2036, 1467, 1253, 845, 675.

Other 4(m,n) (m = 12, 14, 16, n = 1; m = n = 8, 9, 10) were prepared following the same procedure for 4(10,1).

Dodecyldimethylsilylacetylene 4(12,1)

Yield (95.7%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.37 (s, 1H, -C*H*), 1.40-1.25 (m, 20H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>), 0.68-0.59 (m, 2H, Si-C*H*<sub>2</sub>-), 0.17 (s, 6H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 3295, 2958, 2925, 2854, 2036, 1467, 1252, 845, 673.

Dimethyltetradecylsilylacetylene 4(14,1)

Yield (93.9%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.37 (s, 1H, -C*H*), 1.42-1.25 (m, 24H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 3H, -C*H*<sub>3</sub>), 0.67-0.59 (m, 2H, Si-C*H*<sub>2</sub>-), 0.17 (s, 6H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 3295, 2957, 2925, 2854, 2036, 1467, 1251, 844, 673.

Hexadecyldimethylsilylacetylene 4(16,1)

Yield (87.3%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.37 (s, 1H, -C*H*), 1.44-1.25 (m, 28H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 3H, C*H*<sub>3</sub>), 0.69-0.60 (m, 2H, Si-C*H*<sub>2</sub>-), 0.17 (s, 6H, Si-C*H*<sub>3</sub>); IR (neat):  $V_{\text{max}}$  (cm<sup>-1</sup>) = 3295, 2959, 2925, 2854, 2036, 1467, 1252, 845, 673.

#### Methyldioctylsilylacetylene **4**(8,8)

Yield (61.0%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.37 (s, 1H, -C*H*), 1.43-1.24 (m, 24H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, C*H*<sub>3</sub>), 0.66-0.58 (m, 4H, Si-C*H*<sub>2</sub>-), 0.19 (s, 3H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 3295, 2958, 2925, 2855, 2036, 1467, 1254, 1077, 807, 673.

#### Methyldinonylsilylacetylene 4(9,9)

Yield (82.7%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.36 (s, 1H, -C*H*), 1.44-1.25 (m, 28H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, C*H*<sub>3</sub>), 0.67-0.58 (m, 4H, Si-C*H*<sub>2</sub>-), 0.13 (s, 3H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 3294, 2957, 2924, 2854, 2035, 1466, 1253, 809, 672.

#### Didecylmethylsilylacetylene 4(10,10)

Yield (91.3%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.37 (s, 1H, -C*H*), 1.45-1.21 (m, 32H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, C*H*<sub>3</sub>), 0.67-0.58 (m, 4H, Si-C*H*<sub>2</sub>-), 0.13 (s, 3H, Si-C*H*<sub>3</sub>); IR (neat):  $V_{\text{max}}$  (cm<sup>-1</sup>) = 3294, 2958, 2925, 2855, 2035, 1466, 1253, 807, 672.

4. Synthesis of 4-(4-Bromophenyl)-2-methyl-3-butyn-2-ol 7



Under nitrogen, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (70.2 mg, 0.100 mmol), PPh<sub>3</sub> (53.4 mg, 0.204 mmol),  $Pr_2NH$  (50 mL), 2-methyl-3-butyn-2-ol (1.85 g, 22.0 mmol) and CuI (19.8 mg, 0.104 mmol) were added to 1,4-dibromobenzene (4.72 g, 20.0 mmol) in dry THF (100 mL). After stirring at 60 °C for 5 h, the reaction mixture was cooled to rt and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give an orange liquid. The residue was purified by silica gel column chromatography with hexane/AcOEt (v/v, 4/1) to give a white powder (3.49 g, 14.6 mmol, 73.0%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.43 (dt,  $J_I$  = 8.7 Hz,  $J_2$  = 2.1 Hz, 2H, Ar-H), 7.27 (dt,  $J_I$  = 8.7 Hz,  $J_2$  = 2.1 Hz, 2H, Ar-H), 2.15 (br, 1H, -OH), 1.61 (s, 6H, -C $H_3$ ); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 133.2, 131.6, 122.6, 121.8, 95.0, 81.3, 65.8, 31.5; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 3267, 2982, 1486, 1375, 1268, 1164, 1071, 1011, 964, 904, 822.



5. Synthesis of 2-Methyl-4-{4-[(trialkylsilyl)ethynyl]phenyl}-3-butyn-2-ol **8**(m,n)

Typical procedure for the synthesis of  $\mathbf{8}(m,n)$ 

4-{4-[(Decyldimethylsilyl)ethynyl]phenyl}-2-methyl-3-butyn-2-ol 8(10,1)

Under nitrogen, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (35.5 mg, 50.6 µmol), PPh<sub>3</sub> (26.1 mg, 99.5 µmol),  ${}^{4}Pr_{2}NH$  (10 mL), **3**(10,1) (1.24 g, 5.51 mmol) and CuI (18.6 mg, 97.7 µmol) were added to **7** (1.21 mg, 5.07 mmol) in dry THF (10 mL) at rt. After refluxing for 13 h, the reaction mixture was cooled to rt and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a brown liquid. The residue was purified by silica gel column chromatography with hexane/chloroform (v/v, 1/1) to give a yellow liquid (1.86 g, 4.87 mmol, 96.1%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.40-7.32 (m, 4H, Ar-*H*), 2.05 (s, 1H, -O*H*), 1.61 (s, 6H, -C*H*<sub>3</sub>), 1.43-1.27 (m, 10H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>), 0.71-0.65 (m, 2H, Si-C*H*<sub>2</sub>-), 0.21 (s, 6H, Si-C*H*<sub>3</sub>).

Other 8(m,m) (m = 8, 9, 10) were prepared following the same procedure for 8(10,1).

4-{4-[(Methyldioctylsilyl)ethynyl]phenyl}-2-methyl -3-butyn-2-ol 8(8,8)

Yield (76.6%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.40-7.31 (m, 4H, Ar-*H*), 2.20 (br, 1H, -O*H*), 1.61 (s, 6H, -C*H*<sub>3</sub>), 1.48-1.26 (m, 24H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, -C*H*<sub>3</sub>), 0.72-0.64 (m, 4H, Si-C*H*<sub>2</sub>-), 0.18 (s, 3H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 131.9, 131.5, 123.3, 122.8, 105.4, 95.7, 95.3, 81.9, 65.8, 33.5, 32.1, 31.5, 29.4, 24.0, 22.8, 14.8, 14.3, -3.3; IR (neat):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 3349, 2955, 2923, 2853, 2156, 1505, 1466, 1167, 840, 809.

#### 4-{4-[(Methyldinonylsilyl)ethynyl]phenyl}-2-methyl -3-butyn-2-ol 8(9,9)

Yield (98.4%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.40-7.31 (m, 4H, Ar-*H*), 2.02 (br, 1H, -O*H*), 1.61 (s, 6H, -C*H*<sub>3</sub>), 1.48-1.24 (m, 28H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, -C*H*<sub>3</sub>), 0.70-0.64 (m, 4H, Si-C*H*<sub>2</sub>-), 0.18 (s, 3H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.0, 131.6, 123.3, 122.8, 105.4, 95.7, 95.3, 82.0, 65.8, 33.5, 32.1, 31.6, 29.8, 29.5, 24.0, 22.9, 14.9, 14.3, -3.3; IR (neat):  $v_{max}$  (cm<sup>-1</sup>) = 3348, 2956, 2924, 2854, 2156, 1504, 1465, 1166, 839, 806.

#### 4-{4-[(Didecylmethylsilyl)ethynyl]phenyl}-2-methyl -3-butyn-2-ol 8(10,10)

Yield (83.0%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.40-7.30 (m, 4H, Ar-*H*), 2.20 (br, 1H, -O*H*), 1.61 (s, 6H, -C*H*<sub>3</sub>), 1.48-1.24 (m, 32H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 6H, -C*H*<sub>3</sub>), 0.72-0.64 (m,

4H, Si-C*H*<sub>2</sub>-), 0.18 (s, 3H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 131.9, 131.5, 123.3, 122.8, 105.4, 95.7, 95.3, 81.9, 65.8, 33.5, 32.1, 31.5, 29.8, 29.5, 24.0, 22.8, 14.8, 14.3, -3.3; IR (neat): *ν*<sub>max</sub> (cm<sup>-1</sup>) = 3348, 2956, 2924, 2853, 2156, 1504, 1466, 1167, 840, 810.

6. Synthesis of 1-Ethynyl-4-[(trialkylsilyl)ethynyl]benzene 2(m,n)



Typical procedure for the synthesis of 2(m,n)

1-[(Decyldimethylsilyl)ethynyl]-4-ethynylbenzene **2**(10,1)

Under nitrogen, NaOH powder (99.1 mg, 2.48 mmol) was added to **8**(10,1) (1.86 g, 4.85 mmol) in toluene (20 mL) and refluxed for 4 h. The reaction mixture was cooled at room temperature and filtered through celite. The filtrate was washed with 1 N HCl *aq.* and water and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane to give a colorless liquid (1.12 g, 3.46 mmol, 71.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.41 (s, 4H, Ar-*H*), 3.15 (s, 1H, -C*H*), 1.48-1.22 (m, 24H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 3H, -C*H*<sub>3</sub>), 0.71-0.66 (m, 2H, Si-C*H*<sub>2</sub>-), 0.22 (s, 6H, Si-C*H*<sub>3</sub>).

Other 2(m,n) (m = n = 8, 9, 10) were prepared following the same procedure for 2(10,1).

1-Ethynyl-4-[(methyldioctylsilyl)ethynyl]benzene **2**(8,8)

Yield (82.0%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.41 (s, 4H, Ar-*H*), 3.15 (s, 1H, -C*H*), 1.48-1.23 (m, 24H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.9 Hz, 6H, -C*H*<sub>3</sub>), 0.72-0.64 (m, 4H, Si-C*H*<sub>2</sub>-), 0.18 (s, 3H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.0, 131.1, 123.9, 122.1, 105.2, 95.7, 83.4, 79.0, 33.5, 32.1, 31.8, 29.5, 29.4, 24.0, 22.9, 14.8, 14.3, -3.3; IR (neat): *v*<sub>max</sub> (cm<sup>-1</sup>) = 3306, 2956, 2924, 2853, 2157, 1495, 1466, 1252, 839, 803.

1-Ethynyl-4-[(methyldinonylsilyl)ethynyl]benzene 2(9,9)

Yield (93.7%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.41 (s, 4H, Ar-*H*), 3.16 (s, 1H, -C*H*), 1.48-1.23 (m, 28H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, -C*H*<sub>3</sub>), 0.73-0.63 (m, 4H, Si-C*H*<sub>2</sub>-), 0.19 (s, 3H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 3307, 2956, 2924, 2854, 2157, 1495, 1466, 1252, 840, 803.

1-[(Didecylmethylsilyl)ethynyl]-4-ethynylbenzene **2**(10,10)

Yield (89.1%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.41 (s, 4H, Ar-*H*), 3.16 (s, 1H, -C*H*), 1.50-1.23 (m, 32H, -C*H*<sub>2</sub>-), 0.88 (t, *J* = 6.6 Hz, 6H, -C*H*<sub>3</sub>), 0.73-0.63 (m, 4H, Si-C*H*<sub>2</sub>-), 0.17 (s, 3H, Si-C*H*<sub>3</sub>); IR (neat):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 3305 2925, 2854, 2157, 1495, 1466, 1251, 839, 803.

#### 7. Synthesis of Triphenylene 9



In a quartz vessel,  $\sigma$  terphenyl (12.5 g, 54.3 mmol), I<sub>2</sub> (12.5 g, 49.3 mmol) and benzene (1.0 l) was added and irradiated with UV light of the low-pressure mercury lamp for 1 week. The reaction mixture was washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *aq.* and water. The organic layer was dried over *anhyd.* Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was recrystallized from ethanol to give colorless needles (7.92 g, 34.7 mmol, 63.9%). M.p. 201.9-202.5 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.65 (dd,  $J_1$  = 6.3 Hz,  $J_2$  = 3.3 Hz, 6H, Ar-*H*), 7.65 (dd,  $J_1$  = 6.3 Hz,  $J_2$  = 3.3 Hz, 6H, Ar-*H*).

8. Synthesis of 2,3,6,7,10,11-Hexabromotriphenylene 1<sup>[24]</sup>



Under nitrogen, bromine (9.0 mL, 349 mmol) was added dropwise to **9** (3.95 g, 17.3 mmol) and Fe (410 mg, 7.34 mmol) in nitrobenzene (200 mL) with stirring at rt for 20 min and furthermore at 210 °C for 3 h. After cooling the reaction mixture to room temperature, Et<sub>2</sub>O was added and the precipitate was collected. The solid was washed thoroughly with Et<sub>2</sub>O, acetone, and CHCl<sub>3</sub> to give white powder (11.5 g, 16.4 mmol, 94.8%). M.p. >300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.72 (s, 6H, Ar-*H*); IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 1585, 1551, 1454, 1365, 1119, 873, 863.

9. Synthesis of 2,3,6,7,10,11·Hexakis(trialkylsilylethynylphenylethynyl)triphenylene **TPSi**(m,n)



Typical procedure for the synthesis of **TPSi**(m,n)

2,3,6,7,10,11-Hexakis{4-[(methyldioctylsilyl)ethynyl]phenylethynyl}triphenylene **TPSi**(8,8)

Under nitrogen, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (28.7 mg, 40.8 µmol), PPh<sub>3</sub> (21.1 mg, 80.3 µmol), **6**(8,8) (654 mg, 1.67 mmol),  $Pr_2NH$  (10 mL) and CuI (7.58 mg, 39.8 µmol) were added to **1** (140 mg, 200 µmol) in dry toluene (10 mL). After stirring at 60 °C for 17 h, the reaction mixture was cooled to rt and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a dark brown liquid. The residue was purified by silica gel column chromatography with hexane and hexane/chloroform (v/v, 1/1) and by TLC hexane/chloroform (v/v, 5/1) to give a yellow solid (315 mg, 122 µmol, 61.0%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.69 (s, 6H, Ar-*H*), 7.57 (d, *J* = 8.4 Hz, 12H, Ar-*H*), 7.48 (d, *J* = 8.4 Hz, 12H, Ar-*H*), 1.51-1.23 (m, 144H, -C*H*<sub>2</sub>-), 0.89 (t, *J* = 6.9 Hz, 36H, -C*H*<sub>3</sub>), 0.77-0.67 (m, 24H, Si-C*H*<sub>2</sub>-), 0.28 (s, 18H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.8, 128.6, 127.2, 124.8, 123.79, 123.1, 105.5, 95.9, 94.7, 90.3, 33.6, 32.1, 29.5, 24.1, 22.9, 14.9, 14.3, -3.2; IR (KBr): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2922, 2853, 2155, 1510, 1466, 1410, 1250, 835; Anal. Calcd for C<sub>180</sub>H<sub>252</sub>Si<sub>6</sub>: C, 83.65; H, 9.82%. Found: C, 83.61; H, 9.88%.

#### Other **TPSi**(m,n) were prepared following the same procedure for **TPSi**(8,8).

2,3,6,7,10,11-Hexakis{4-[(dinonylmethylsilyl)ethynyl]phenylethynyl}triphenylene **TPSi**(9,9) Yield (47.2%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.79 (s, 6H, Ar-*H*), 7.58 (d, *J* = 8.7 Hz, 12H, Ar-*H*), 7.48 (d, *J* = 8.7 Hz, 12H, Ar-*H*), 1.50-1.23 (m, 168H, -C*H*<sub>2</sub>-), 0.89 (t, *J* = 6.9 Hz, 36H, -C*H*<sub>3</sub>), 0.75-0.66 (m, 24H, Si-C*H*<sub>2</sub>-), 0.21 (s, 18H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.8, 128.6, 127.3, 124.9, 123.8, 123.1, 105.5, 95.9, 94.7, 90.3, 33.6, 32.1, 29.8, 29.6, 24.1, 22.9, 14.9, 14.3, -3.2; IR (KBr): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2923, 2853, 2154, 1510, 1466, 1410, 1250, 835; Anal. Calcd for C<sub>192</sub>H<sub>276</sub>Si<sub>6</sub>: C, 83.77; H, 10.11%. Found: C, 83.73; H, 10.16%. 2,3,6,7,10,11-Hexakis{4-[(didecylmethylsilyl)ethynyl]phenylethynyl}triphenylene **TPSi**(10,10) Yield (41.7%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.59 (s, 6H, Ar-*H*), 7.56 (d, *J* = 8.4 Hz, 12H, Ar-*H*), 7.47 (d, *J* = 8.4 Hz, 12H, Ar-*H*), 1.52-1.22 (m, 192H, -C*H*<sub>2</sub>-), 0.89 (t, *J* = 6.6 Hz, 36H, -C*H*<sub>3</sub>), 0.78-0.69 (m, 24H, Si-C*H*<sub>2</sub>-), 0.24 (s, 18H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.7, 128.7, 127.4, 124.9, 123.8, 123.1, 105.5, 95.9, 94.7, 90.3, 33.6, 32.1, 29.9, 29.8, 29.6, 24.1, 22.9, 14.9, 14.3, -3.3; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 2922, 2853, 2149, 1465, 1418, 1249, 1003, 868, 840; Anal. calcd for C<sub>204</sub>H<sub>300</sub>Si<sub>6</sub>: C, 83.88; H, 10.35%. found: C, 83.50; H, 10.35%.

2,3,6,7,10,11-Hexakis{4-[(decyldimethylsilyl)ethynyl]phenylethynyl}triphenylene **TPSi**(10,1) Yield (70.4%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.31 (s, 6H, Ar-*H*), 7.48 (d, *J* = 8.4 Hz, 12H, Ar-*H*), 7.42 (d, *J* = 8.4 Hz, 12H, Ar-*H*), 1.56-1.26 (m, 96H, -C*H*<sub>2</sub>-), 0.89 (t, *J* = 6.6 Hz, 18H, -C*H*<sub>3</sub>), 0.80-0.72 (m, 12H, Si-C*H*<sub>2</sub>-), 0.30 (s, 36H, Si-C*H*<sub>3</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 132.2, 131.8, 128.3, 127.2, 124.3, 123.6, 123.2, 105.2, 96.3, 94.6, 90.5, 33.6, 32.1, 29.9, 29.6, 24.0, 22.9, 16.4, 14.3, -1.5; IR (KBr): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2924, 2853, 2156, 1510, 1466, 1415, 1250, 1016, 879, 835.

10. Synthesis of meso-1,2-Dibromo-1,2-diphenylethane 10<sup>[25]</sup>



Bromine (3.0 mL, 58.6 mmol) was added dropwise to *trans*-stilbene (8.95 g, 49.6 mmol) in diethyl ether (200 mL) at rt. After stirring for 1 h, the precipitate was collected and washed thoroughly with diethyl ether to give white powder (15.7 g, 46.2 mmol, 93.1%). M.p. 244.8 ~ 246.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.55-7.49 (m, 4H, Ar-*H*), 7.46-7.33 (m, 6H, Ar-*H*), 5.48 (s, 2H, -C*H*); IR (KBr):  $v_{\text{max}}$  (cm<sup>-1</sup>) = 1496, 1452, 1136, 763, 691, 601, 552.

11. Synthesis of Diphenylacetylene 11<sup>[25]</sup>



Potassium hydroxide (21.6 g, 385 mmol) was dissolved completely in ethanol (36 mL) by heating. To the solution, **10** (14.7 g, 43.3 mmol) was added little by little and the mixture was refluxed for 2 days. The hot mixture was poured into cold water (400 mL) and the precipitate was collected. It was dissolved in hexane and washed with *sat.* NaCl *aq.* The organic layer was dried over *anhyd.* Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduce pressure. The residue was recrystallized from ethanol (6.0 mL) to give colorless needles (5.77 g, 32.4 mmol, 74.8%). M.p. 61.3 ~ 62.1 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.58-7.50 (m, 4H, Ar-*H*), 7.40-7.32 (m, 6H, Ar-*H*); IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 3062, 1600, 1463, 1442, 1069, 917, 756, 689, 510.

12. Synthesis of 1,2,3,4,5,6-Hexaphenylbenzene **12**<sup>[26]</sup>



The solution of **11** (6.08 g, 34.1 mmol) and PdCl<sub>2</sub>(PhCN)<sub>2</sub> (184 mg, 481 µmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was stirred for 2 days. The resulting precipitate was filtered and washed with DMF to give white crystalline powder (3.21 g, 6.01 mmol, 52.9%). M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 6.84 (s, 30H, Ar-H); IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 3024, 1600, 1496, 1441, 1401, 1073, 1028, 782, 729, 694, 554.

Synthesis of 1,2,3,4,5,6-Hexakis(4-iodophenyl)benzene 13<sup>[27]</sup>



The mixture of **12** (887 mg, 1.66 mmol), PIFA (Planar Inverted F Antenna: bis(trifluoroacetoxy)iodobenzene) (2.41 g, 5.59 mmol) and iodine (1.37 g, 5.41 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) under nitrogen was stirred at room temperature for 21 h in the dark, and then hexane was added to the reaction mixture. The resulting precipitate was filtered and washed with hexane. This solid was dissolved in CHCl<sub>3</sub> and washed with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> *aq.* and *sat.* NaCl *aq.* The organic layer was dried over *anhyd.* Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduce pressure. The residue was recrystallized from CHCl<sub>3</sub>-hexane to give a white solid (1.57 g, 1.21 mmol, 72.9%). M.p. > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.06 (d, *J* = 8.4 Hz, 12H, Ar-*H*); IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 1487, 1386, 1138, 1059, 1006, 822, 760.





To the solution of **13** (3.64 g, 2.82 mmol) in dry  $CH_2Cl_2$  (1.2 L) was added dropwise FeCl<sub>3</sub> (11.2 g, 69.1 mmol) in  $CH_3NO_2$  (19 mL) over 10 min. After stirring for 6.5 h, the reaction was quenched by MeOH (ml). The yellow precipitate was filtered through a membrane filter, washed with  $CHCl_3$  and MeOH until the filtrate was colorless and dried under reduced pressure to give yellow powder (3.32 g, 2.60 mmol, 92.2%). M.p. >300 °C; IR (KBr):  $v_{max}$  (cm<sup>-1</sup>) = 1562, 1347, 843.

Synthesis of 2,5,8,11,14,17-Hexakis[(trialkylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene HBCSi(m)



Typical procedure for the synthesis of **HBCSi**(m)

2,5,8,11,14,17-Hexakis[(decyldimethylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(10)

Under nitrogen,  $PdCl_2(PPh_3)_2$  (15.07 mg, 21.5 µmol),  $PPh_3$  (11.12 mg, 42.4 µmol), 4(10,1) (404 mg, 1.80 mmol),  $Pr_2NH$  (4.0 mL) and CuI (5.52 mg, 29.0 µmol) were added to the solution of **3** (256 mg, 200 µmol) in dry toluene (4.0 mL). After stirring at 50 °C for 5 h, the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure to give a reddish brown liquid. The residue was washed with AcOEt several times to get an orange solid. The solid was further purified by preparative GPC (JAIGEL-1H/2H, CHCl<sub>3</sub>) to give **HBCSi**(10) an orange-yellow sticky wax-like solid (609 mg, 0.319 mmol, 52.8%). MS (MALDI-TOF, DHB) m/z (%): 1855.92 [M+H]+; Anal. Calcd for C<sub>126</sub>H<sub>174</sub>Si<sub>6</sub>: C, 81.48; H, 9.44%. Found: C, 81.46; H, 9.46%.

Other **HBCSi**(m) were prepared following the same procedure for **HBCSi**(10).

2,5,8,11,14,17-Hexakis[(dodecyldimethylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(12)

Yield (58.8%: sticky wax-like solid); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.65 (br, 12H, Ar-H), 1.76-1.12 (m, 120H, -C*H*<sub>2</sub>-), 1.03 (br, 12H, Si-C*H*<sub>2</sub>-), 0.78 (t, *J* = 6.9 Hz, 18H, -C*H*<sub>3</sub>), 0.61 (br, 36H, Si-C*H*<sub>3</sub>); IR (KBr): <sub>*V*max</sub> (cm<sup>-1</sup>) = 2922, 2852, 2151, 1604, 1466, 1366, 1248, 1004, 868, 840; MS (MALDI-TOF, DHB) *m/z*: 2024.18 [M+H]+. 2,5,8,11,14,17-Hexakis[(dimethyltetradecylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(14)

Yield (45.6%: sticky wax-like solid); MS (MALDI-TOF, DHB) *m*/*z* (%): 2192.36 [M+H]+; Anal. Calcd for C<sub>150</sub>H<sub>222</sub>Si<sub>6</sub>: C, 82.12; H, 10.20%. Found: C, 82.26; H, 10.26%.

2,5,8,11,14,17-Hexakis[(hexadecyldimethylsilyl)ethynyl]hexa-*peri*-hexabenzocoronene **HBCSi**(16)

Yield (42.9%: sticky wax-like solid); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.66 (br, 12H, Ar-*H*), 1.78-0.95 (m, 168H, -C*H*<sub>2</sub>-), 0.79 (t, *J* = 6.9 Hz, 18H, -C*H*<sub>3</sub>), 0.61 (br, 36H, Si-C*H*<sub>3</sub>); IR (KBr): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2922, 2852, 2150, 1603, 1468, 1366, 1248, 1004, 868, 830; MS (MALDI-TOF, DHB) *m/z*: 2360.44 [M+H]+; Anal. Calcd for C<sub>162</sub>H<sub>246</sub>Si<sub>6</sub>: C, 82.37; H, 10.50%. Found: C, 82.35; H, 10.61%.

15

Compound	Lattice	Spacing (Å)		Miller indices
(Mesophase)	constants (Å)	Observed	Calculated	hkl
<b>TPSi</b> (10,1)	a = 36.1	31.1	31.2	100
at 180 $^{\circ}\mathrm{C}$		18.1	18.0	110
	M = 2163.64	15.8	15.6	200
$\operatorname{Col_h}$	$Z^{a} = 1.1$	11.8	11.8	210
		4.9	-	hch
<b>TPSi</b> (8,8)	a = 59.3	32.5	32.5	110
at 100 °C	b = 38.8	29.6	29.7	200
		14.8	14.8	400
$Col_r(C2/m)$	M = 2584.44	9.88	9.88	600
	$Z^{b} = 2.0$	4.7		hch
<b>TPSi</b> (9,9)	a = 62.7	33.7	33.7	110
at 100 °C	b = 40.0	31.5	31.3	200
		16.8	16.8	220
$Col_r(C2/m)$	M = 2752.76	15.7	15.7	400
	$Z^{b} = 2.0$	13.0	13.0	130
		12.0	12.0	510
		10.4	10.4	600
		4.8	-	hch
<b>TPSi</b> (10,10)	a = 63.9	34.5	34.5	110
at 100 °C	b = 41.0	32.0	31.9	200
		16.0	16.0	400
$Col_r(C2/m)$	M = 2921.08	10.6	10.6	600
	$Z^{b} = 2.0$	4.7	-	hch

Table S1. X-ray diffraction data of **TPSi**(m,n) (m = 8, 9, and 10; n = 1, 8, 9, and 10).

<sup>*a*</sup>Calculated assuming that the density and the stacking distance were 1.0 g cm<sup>-3</sup> and 3.5 Å, respectively.

 $^b\mathrm{Calculated}$  assuming that the density and the stacking distance were 1.0 g cm  $^3$  and 3.7 Å, respectively.

formula	$\mathrm{C}_{102}\mathrm{H}_{96}\mathrm{O}_{2}\mathrm{Si}_{6}$
formula weight	1522.33
temperature (K)	150
crystal size (mm)	$0.85 \times 0.06 \times 0.05$
crystal system	monoclinic
space group	<i>C</i> 2/c
a (Å)	28.295(8)
b (Å)	39.941(11)
<i>c</i> (Å)	8.314(2)
α (°)	90
β(°)	100.421(4)
γ(°)	90
V (Å <sup>3</sup> )	9241(4)
Ζ	4
Dc (g/cm <sup>3</sup> )	1.094
μ (mm <sup>-1</sup> )	0.137
$ heta_{\min/\max}$ (°)	0.89/25.00
$R_1 \left[ F_0 > 2\sigma(F_0) \right]$	0.1214
$wR_2$ (all F <sub>0</sub> <sup>2</sup> )	0.3302
GOF	1.174
measured reflns	20795
independent reflns	8131
observed reflns	3051
reflns used	8131
parameters	507
	1057416

Table S2. Single crystal X-ray analysis data of TPSi(1,1).

Compound	Lattice	Spacing (Å)		Miller indices
(Mesophase)	constants (Å)	Observed	Calculated	hkl
<b>HBCSi</b> (10)	<i>a</i> = 31.4	26.6	27.2	100
at 100 $^{\circ}\mathrm{C}$	h = 3.5	15.5	15.7	110
		13.4	13.6	200
$\operatorname{Col}_{h}$	M = 1857.24	10.2	10.3	210
	$Z^{a} = 0.97$	8.93	9.06	300
		6.80	6.80	400
		4.53	4.53	600
		4.5	-	hсн
		3.5		h
<b>HBCSi</b> (12)	a = 32.8	28.1	28.4	100
at 100 $^{\circ}\mathrm{C}$	h = 3.5	16.5	16.4	110
		14.2	14.2	200
$\operatorname{Col}_{h}$	M = 2025.56	10.8	10.8	210
	$Z^{a} = 1.0$	9.48	9.48	300
		4.5	<u> </u>	hch
		3.5	<b>y</b> -	h
<b>HBCSi</b> (14)	a = 34.5	29.6	29.9	100
at $100~^\circ\mathrm{C}$	h = 3.6	17.2	17.3	110
		14.8	15.0	200
$\operatorname{Col}_{h}$	M = 2193.88	11.3	11.8	210
	$Z^{a} = 1.0$	9.97	9.97	300
		4.5	-	hCH
		3.6	-	h
				100
HBCSi(16)	a = 35.3	30.4	30.6	100
at 100 °C	h = 3.5	17.7	17.5	110
0.1		15.4	15.3	200
$\operatorname{Col_h}$	M = 2362.20	10.2	10.2	300
	$Z^a = 0.96$	6.11	6.11	500
$\rightarrow$		4.5	-	hCH
	1	3.5	-	h

Table S3. X-ray diffraction data of HBCSi(m) (m = 8, 10, 12, 14, and 16).

<sup>a</sup>Calculated assuming that the density was ~1.0 g cm<sup>·3</sup>.



Figure S2. POM textures of a) **TPSi**(9,9) at 152 °C, b) **HBCSi**(14) at 150 °C, and c) **HBCSi**(16) at 150 °C.



Figure S3. XRD pattern of **TPSi**(9,9) at 100 °C.



Figure S4. XRD pattern of **TPSi**(10,10) at 100 °C.



Figure S5. XRD pattern of **HBCSi**(12) at 100 °C.



Figure S6. XRD pattern of **HBCSi**(14) at 100 °C.



Figure S7. XRD pattern of HBCSi(16) at 100 °C.



Figure S8. Electric field dependence of the hole mobility in  $Col_h$  phase of **HBCSi**(12) at 140 °C. The sample thickness was 5  $\mu$ m.



Figure S9. The UV-vis (a) and Emission (b) spectra of **TPSi**(9,9) ( $\lambda_{ex}$ : 363 nm). In dry CH<sub>2</sub>Cl<sub>2</sub>, 1 × 10<sup>-7</sup> M.



Figure S10. The UV-vis (a) and Emission (b) spectra of **HBCSi**(14) ( $\lambda_{ex}$ : 380 nm). In dry CH<sub>2</sub>Cl<sub>2</sub>, 1 × 10<sup>-6</sup> M.